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EXECUTIVE SUMMARY

INSPECTION OF ELASTOMERIC COMPONENTS FROM PRESSURE RELIEF VALVE NO 10, IN PRESSURE RELIEF DUCT, BRUCE A NGS

D.C. Cordingley

The elastomeric components from this valve were examined for deterioration, damage, and cause of leakage. The small change in the durometer hardness since installation indicates the absence of oxidative aging. An eight point difference in hardness between the top and bottom diaphragms suggests the presence of different formulations and/or curing during manufacture.

Elastomeric deterioration in the diaphragms includes (i) separations from inadequate fusion at the junction of adjacent sections of rubber, (ii) typical ozone induced surface cracking at the stressed bent section adjacent to the flange, and (iii) permanent set of the 1.8 mm high elastomer flow into the oval shaped bolt holes of the blow-back limiting fixture. The mechanical damage includes slits and gouges to the fabric in the cover rubber, cutting of strips from the flange, obliteration of sections of moulded corners, and enlargement and mis-placement of bolt holes. Leakage trail residues on the upper diaphragm were found on both sides of the clamping flange. The above conditions and the 5 mm deep channel found in the elastomeric D-seal at the seating/sealing junction not only necessitated replacement of the diaphragms and D-seal, but also suggest that the remaining valves need to be examined. The random nature of the mechanical damage and elastomeric deterioration is attributed to shortcomings in manufacture, quality control inspection and installation care. Although the upper bumper ring is in a good condition, the distribution of contact impressions indicates a wobble as the piston is raised and the need for a wider rubber bumper.

[Handwritten initials]

job	file	date	report no.
32-050-018	835.6211	July 1, 1987	87-27-K



ontario hydro research division

To: Mr. R. Coutts
Station Manager
Bruce A NGS

**INSPECTION OF ELASTOMERIC COMPONENTS FROM PRESSURE
RELIEF VALVE NO 10, IN PRESSURE RELIEF DUCT,
BRUCE A NGS**

D.C. Cordingley

The elastomeric components from this valve were examined for deterioration, damage, and cause of leakage. The small change in the durometer hardness since installation indicates the absence of oxidative aging. Elastomeric deterioration in the diaphragms includes separation of adjacent sections of rubber, ozone induced surface cracking and permanent set of the elastomer flow into the blow-back limiting fixture. Mechanical damage includes slits and gouges in the cover rubber, cutting of strips from the flange, obliteration of moulded corners, and enlargement and mis-placement of bolt holes. Leakage trail residues were found on the clamping flange of the upper diaphragm. The above conditions and the deep channel found in the elastomeric D-seal at the seating/sealing junction not only necessitated replacement of the diaphragms and D-seal, but also suggest that the remaining valves need to be examined. Although the upper bumper ring is in a good condition, the distribution of contact impressions indicates a wobble as the piston is raised and the need for a wider rubber bumper.

The elastomeric components of the above pressure relief valve (PRV) including, the two diaphragms, the base seal which contacts the movable piston and the flap valve seal were examined for signs of deterioration and/or damage. The initial order for these diaphragms was placed in May 1971 with Garlock Canada Ltd., Toronto, Ontario, to the requirements of the Ontario Hydro Provisional Specification, "Elastomeric Seals For Relief Valves, Bruce GS," issued October 1970. From a recent review of factory files it appears that the diaphragms were made from an ethylene-

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propylene terpolymer, Compound No. 95802, as specified. The manufacturer's records are reported to show that the initial production mould for the diaphragms stretched resulting in a progressively thicker wall section as successive diaphragms were manufactured. The initial diaphragms were of a poor quality, some are known to have been discarded at or before arrival at Bruce A NGS, whereas other installed diaphragms were replaced at a later date. It is not known if these replacements occurred before or after modification to the valves during the installation of the blow-back limiting fixture to prevent reversal of the diaphragm when the vacuum building is pressurized. The initial shipments of the D-shaped base seal were made from a 35 $\pm$ 5 A durometer hardness type W neoprene stock. The material extruded poorly into an oval shape. This necessitated a reformulation for later shipments in order to obtain the desired cross-section, however the hardness increased to the 40 to 45 A durometer level. The seals and diaphragms on Number 10 PRV were selected for examination as this valve was known to have the highest rate of leakage of all valves in the duct.

Inspection

The valve was removed from the pressure relief duct (PRD), placed in the maintenance service area and dismantled by station personnel. The elastomeric components were examined and the instantaneous durometer hardness measurements made with a Rex A instrument by the method described in ASTM D2240-86, Standard Test Method for Rubber Property - Durometer Hardness. The following conditions were noted:

1. Durometer Hardness of Diaphragms

The data for the durometer hardness of the top and bottom diaphragms presented in Appendix 1 differ by about 8 A units. The bottom diaphragm at 62 A units of hardness is slightly above the specified range of 50 to 60 A units, whereas the upper diaphragm at 54 A units is at the midpoint of the hardness range specified.

2. Damage to Bolt Holes

A considerable number of bolt holes had been damaged from what appeared to be lateral slippage or wandering of the drill while the hole was being bored. On the bottom diaphragm one hundred and eighteen holes were examined. Seventy-five (63.6%) were cleanly cut, twenty-three (19.5%) were damaged to a minor degree and twenty (16.9%) were damaged to a considerable extent. Photographs showing severely damaged bolt holes are presented in Appendix 2.

3. Compression Flow and Splitting of Rubber at Bolt Holes

At the junction of the outer diaphragm flange and the oval shaped bolt holes in the blow-back limiting fixture, the cover rubber has flowed into and filled the cavity which exists between the bolt through the diaphragm and the boundary of the holes on the fixture. The flowed rubber has set to form a mound at the bolt hole. For some bolt holes this compressive flow has exceeded the ultimate elongation properties of the rubber and the flange rubber has split towards the bend in the flange along the flow boundary. Typical flow patterns and splits of this type are shown in the photographs in Appendix 3. This effect when coupled with a badly drilled hole on the opposite face (Appendix 2A) has reduced the sealing length between the bolt hole and the vacuum or containment boundary.

4. Height of Mound at Bolt Holes From Compression Flow and Set of Rubber

Measurements of the difference in thickness of the diaphragm flange at the flowed rubber mound adjacent to the bolt hole, at a similar position on the inner diaphragm flange, and at the mid-point between bolt holes are listed in Appendix 4. The flowed rubber mound is about 1.8 mm higher than the adjacent flange surface.

5. Sealing Distance Between Bolt Hole and Vacuum Boundary

A random sampling of twenty-one clean cut bolt holes on both the inside and outside flanges of the bottom diaphragm found a mean sealing distance between the bolt hole and vacuum boundary of 18.4 mm on the outside flange and 12.8 mm on the inside flange. For the latter a minimum distance of 10 mm was found. The data and analysis of these measurements are listed in Appendix 5.

6. Mechanical Impact Damage

The diaphragms have been mechanically damaged at numerous sites. In the sealing flange area, slits occur in the cover rubber which penetrate to the fabric reinforcement over lengths up to 10 cm. The photographs in Appendix 6 show this type of damage. These types of damage are attributed to mechanical impact from careless handling during shipping and/or installation. Random sections of the flange edge of the diaphragms have been sliced-off, reducing the flange width by up to 1 cm over a circumferential distance of up to 30 cm. This has reduced by up to one-half the distance and amount of seal between the bolt hole and the edge of the seal. The amount of seal removed and the magnitude of the reduction in the seating/sealing surfaces for selected bolt holes are shown in the photographs in Appendix 7.

7. Cracking and Separation Deterioration

Two types of cracking and separation deterioration have occurred at the surface of the diaphragms. The first type of separation is located at both junctions of the moulded bent section and the wall and flange of the diaphragm. On the bottom diaphragm a jagged single circumferential line of separation predominates at the junction of the flange and bend on the convex surface of the bent section. On the upper diaphragm the circumferential cracking has occurred at the concave surface where two or more lines of irregular separation have formed at the junction of the diaphragm wall and the bent section. At the above sites the cracking is perpendicular to the direction of strain (elongation) and up to 1 mm deep. Cracks with this feature which develop in elastomeric products are generally attributed to atmospheric ozone. Photographs of typical crack formations in the diaphragms which are attributed to ozone are presented in Appendices 6A and 8A. The second type of separation is shown in the photographs B, C and D of Appendix 8.

8. Leakage Trails

Although the leakage rate to vacuum at this valve was reported to be 99 L/min, no data are available on the leakage rate from containment at the clamping flanges of the diaphragms. Ample visual evidence of leakage sites from containment was present however on the flanges of the diaphragms. The photographs in Appendix 9 show examples of the different types of leakage trails. Some trails traverse the width of the flanges, others commence at the bolt holes and progress to the inner bend of the diaphragm. The trails are rust thought to have been formed when the PRV was assembled, installed and tested for leakage with water or with a water base soap solution. The distribution of the water induced rust formations between the rubber and metal flange is clear evidence of the absence of any sealing/seating force at these locations. It is particularly significant that, where these trails occur, they cover a considerable area often extending beyond the adjacent second or third bolt holes which by themselves may be leak tight. The rust trails also extend along the outer edge for a distance of up to 0.5 m in length.

9. Loss of Moulded Corners at Bend

During manufacture the right-angled junction of the flange and the wall of the diaphragm was moulded in place to form a distinctive and easily identifiable curvature or bend in the surface of the diaphragm. At random locations this bend has been obliterated on the convex face of the bend, Appendix 9. Adjacent and associated with these obliterations are other imprints, discontinuities and repair patches. These defects also occur opposite many of the major leakage trails. The upper diaphragm with serial number 15U was identified by the manufacturer as one

from the initial production lot. The serial number on the bottom diaphragm was not legible. The presence of what appears to be repair patches adjacent to the obliterated bends suggest that these defects originated prior to installation. The obliterations are of a form which suggests that the diaphragm may have been incompletely cured, then folded or creased during prolonged shipment or storage prior to installation.

10. Vacuum D-Shaped Seal

The diaphragms which flank the piston provide a movable and flexible barrier and seal between the atmosphere of the pressure relief duct and the outside environment atmosphere. The seal between the atmosphere of the pressure relief duct and the vacuum duct is located in a U-channel in the base of the pressure relief valve. A guillotine type circular blade welded to the movable piston seats at the apex of the D-seal. The seating force applied to the D-seal by the rounded 3 mm wide foot consists of the weight of the piston and the atmospheric pressure acting on the top face of the piston. This seating force applied over the narrow contact blade has impinged on the neoprene seal and deformed the seal to a depth of up to 5 mm. A photograph of this groove is shown in Appendix 10. Also tabled are the measurements and analysis of durometer hardness of the neoprene D-seal. The manufacturer reports that the initial attempt to produce this seal to a specified durometer A hardness of 30 to 35 units resulted in extrusion problems which formed an oval shaped seal. The type W neoprene formulation was modified to provide a seal which could be extruded in a D-shape but this increased the durometer hardness to 40±5 units. The present durometer A hardness of 50 units is about 5 units above the upper limit of the production tolerance.

11. Upper Bumper Ring

The rectangular-shaped neoprene upper bumper ring was found to be in a satisfactory condition. The durometer hardness was 47 Shore A units and hence equivalent to the vacuum D-shaped seal in the bottom casing of the valve. These data are tabled in Appendix 11. Photographs of the impact surface on the rubber bumper are also presented. The impact impressions left on the neoprene bumper ring by the upper piston nose indicate a variation in the location of the impact position because of possible wobble by the ascending floating upper piston. These impressions suggest that the impact nose of the upper piston may on occasion miss complete contact with the rubber bumper. Chunks of rubber appear to have been removed at those edge locations where contact by the bumper nose leaves the bumper pad. A rust track on the inside surface of the roof of the upper casing suggests that the impact nose of the upper piston has impacted and chipped the painted metal surface allowing rusting to occur. Obviously, the width of the rubber bumper ring is not wide enough to compensate for the magnitude of wobble in the ascending floating upper piston.

Discussion

The durometer hardness of the top and bottom diaphragms differ by about eight units, and hence indicate the use of two different formulations and/or cure in their manufacture. The hardness of the bottom diaphragm is only slightly above the range specified, whereas the hardness of the top diaphragm is at the mid-point of the range specified. These data suggest that very little chemical oxidative aging has occurred during their sixteen years of service. The slight difference in thickness of the two flanges on the lower diaphragm may confirm the manufacturer's statement that the initial production mould stretched resulting in progressively thicker wall sections as successive diaphragms were manufactured.

The presence of cracking in the surface of the diaphragms at the stressed flange lip was attributed to deterioration induced by atmospheric ozone despite the fact that an ethylene-propylene terpolymer was used in the formulation of these items. For elastomeric materials the time to the appearance of ozone cracking and its magnitude is also a function of the amount of strain (elongation), ozone concentration, temperature, type of elastomer and formulation or presence of antiozonants. Another type of separation has occurred at junctions where the original uncured or partly cured rubber sheets were laid down during fabrication of the diaphragms. These junctions do not appear to have knitted or fused together during curing and may have pulled apart because of aging, the vacuum load, or when flexed during the occasional test of the valve. These defects are indicative of poor quality material and processing. Their effect on the performance and life of the diaphragms is not known.

Several types of mechanical damage have occurred to the diaphragms which lessen one's confidence in their ability to provide a reliable containment envelope and barrier to vacuum. Multiple leakage trails of rust from bolt holes or directly across the flange attest to the presence of leak sites since installation. Damaged sites which have reduced the length of the sealing path across the flange include:

1. Enlarged bolt holes from careless drilling of holes,
2. Impact slits and gouges to the rubber on the flange surface,
3. Deliberate irregular slicing-off of up to 1 cm of the outer rim of the rubber flange over distances up to 30 cm, and
4. Excessive compression load which has caused the rubber to flow into the oval bolt holes of the blow-back limiting fixture causing the flowed rubber to split in the across-flange direction. These mounds will demand a very

precise realignment of every bolt hole of the flexible diaphragm when the components of the PRV are reassembled. Failure to achieve this precision in realignment could introduce leakage paths at the bolt holes.

The obliteration of the moulded convex corners at the right-angled junction of the flange and the wall of the diaphragm and the adjacent imprints, discontinuities and repair patches appear to have occurred before installation. Their association with many of the leakage trails suggests a criterion for assessing the suitability of the spare diaphragms. These defects may be the least conspicuous features of the poor quality diaphragms made and accepted during the initial production runs and may be due to the loss of mould pressure as the mould expanded. Now that these features are known to be associated with leakage, they should be cause for rejection of replacement diaphragms and for new diaphragms presently being ordered for the Darlington NGS.

On the basis of the above mechanical damage and defects it was recommended that the diaphragms be replaced. It is not known if any of these defects are present in the replacement diaphragms.

The mechanical damage and to a lesser extent the elastomeric deterioration previously described are attributed to random events which have occurred during the manufacture and installation of the diaphragms. These factors may interact to intensify and to accelerate the time dependent break down of the diaphragm composite. An analogy may be made by a comparison of these findings with the failed vacuum building roof seal at the Bruce B NGS. Both products are of similar construction. Because the observed defects are essentially random events due to shortcomings in manufacture, quality control inspection, and installation care, similar defects must be assumed for the diaphragms in the remaining valves. The reliability and stability of these valves can only be confirmed by a direct examination of all the diaphragms in the installed valves and replacement of those diaphragms showing similar defects.

Neither the permanent set of the 5 mm deep V-shaped indentation in the vacuum D-shaped neoprene seal nor the 5 unit increase in durometer hardness since installation are of concern. The small increase in durometer hardness indicates that very little oxidative aging has occurred to this seal. However the inability of the station maintenance staff to obtain an exact realignment of this groove and the seating blade when the valve was reassembled resulted in two locations where the circumference of the blade crossed the circumference of the groove. This resulted in two possible leakage paths and as a consequence the D-seal was removed and replaced. During the examination of the spare supply of these seals it was discovered that some had not been spliced. Until jointing moulds and splicing chemicals become available, and a jointing technique is developed, these spares are useless.

The rubber seal in the flap valve was in good condition. The rubber O-ring between the bottom casing of the valve and the floor of the PRD could not be examined as it was used to seal the opening to vacuum during the maintenance period.

The spare elastomeric parts are coiled and stored at one end of the turbine floor. These areas are known to have abnormally high concentrations of ozone in the air from ozone produced by the electrical generators. Stressed (coiled) elastomeric parts are therefore sensitive to this condition. Although the diaphragms are stored in plastic bags not all bags are air tight. All rubber spare parts should be re-bagged and stored in a temperature controlled area known to have only normal concentrations of atmospheric ozone.

Conclusions

The ethylene-propylene diaphragms and neoprene seals on the PRV examined do not show any significant signs of oxidative aging. Age dependent deterioration in the diaphragms includes surface cracking from atmospheric ozone, and separation of the cover rubber from inadequate fusion at the junction of adjacent sections of rubber. Both are stress effects induced primarily by the vacuum load.

Mechanical damage is widespread and is attributed to shortcomings in manufacture, quality control inspection, and installation care. In any case, the known leakage and the magnitude and number of leakage trails attest to an inadequate sealing system in the PRV. These conditions suggest that the remaining valves need to be examined. A wider rubber bumper in the upper casing of the valve is required to compensate for the wobble in the rising piston.

Improved inventory control of spare elastomeric components and provision of improved storage conditions are required to ensure immediate availability of replacement parts.

Approved by:

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Chemical Research Dept

Prepared by:

[Signature]

for D.C. Cordingley
Chemist - Materials Research
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Reviewed by:

R.W. Glass

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Supervising Chemist
Materials Chemistry Section

DCC:em

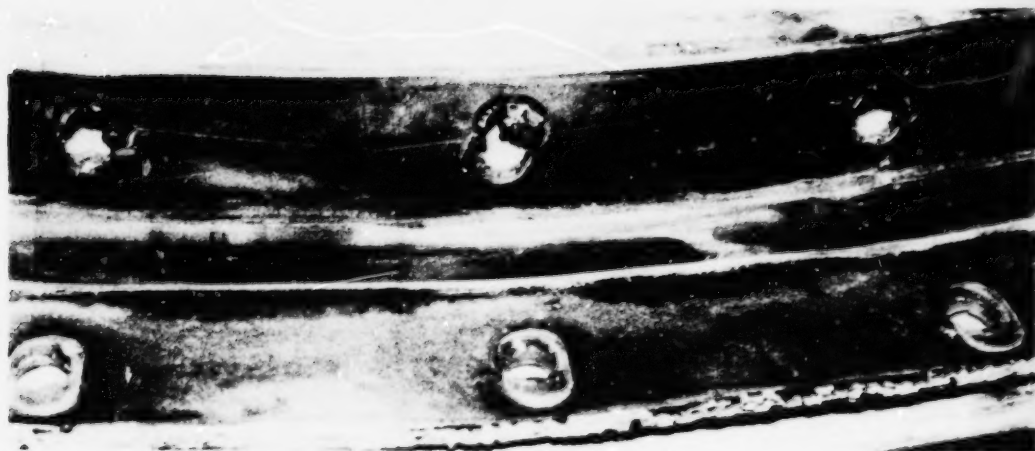
APPENDIX 1

Data For Durometer Hardness of Upper and Lower Diaphragms From
No. 10 Pressure Relief Valve, Pressure Relief Duct, Bruce A NGS.

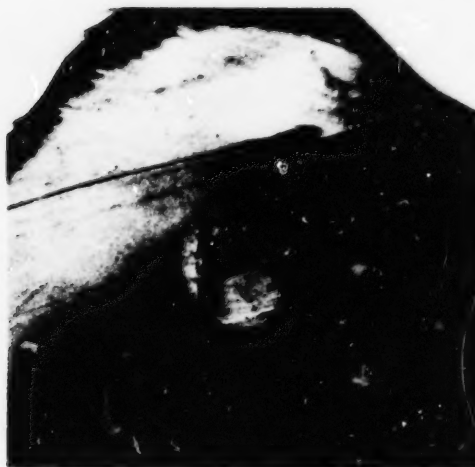
Measurement Number	Durometer Hardness, REX A, ASTM D 2240						
	Bottom Diaphragm			Upper Diaphragm			
	Inner Flange	Outer Flange	Middle Outside	Inner Flange	Outer Flange	Middle Inside	Middle Outside
1	61	63	62	54	57	57	53
2	62	63	62	53	54	56	56
3	64	62	66	51	57	56	56
4	63	64	59	52	58	56	55
5	63	65	64	52	55	56	52
6	67	60	63	51	55	55	54
7	61	63	68	53	54	55	52
8	63	63	64				
9	63	61	72				
10	61	61	70				
11	67	62	62				
12	61	59	60				
13	59	60	62				
14	65	60	62				
15	59	60	55				
16	59	62	66				
17	63	63	60				
18	62	62	63				
19	61	63	64				
20	63	63	59				
21	62	60	63				
Mean $\bar{X}$	62.3	61.9	63.1	52.3	55.7	55.9	54.0
Standard Deviation:							
ON	2.17	1.55	3.75	1.03	1.48	0.64	1.60
ON-1	2.22	1.59	3.84	1.11	1.60	0.69	1.73

Photographs Showing Severe
Of Elastomeric Diaphragms
Pressure Relief

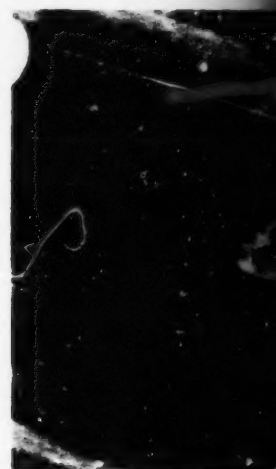
A



C



D



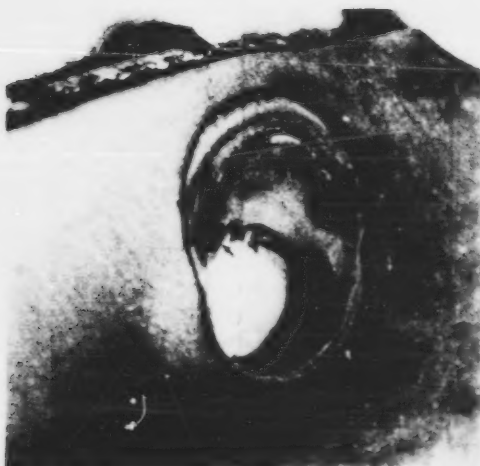
2

ged Bolt Holes in Flange
ssure Relief Valve No 10,
Bruce A NGS.

B



E



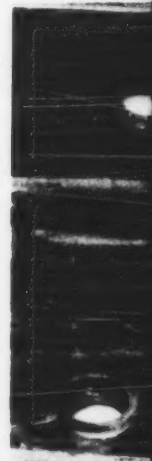
APR

Photographs Showing Type
And Splitting of Flowed Rock
Which Resulted in a Reduced
Surface Between The Bolt Head
Diaphragms From No 10 Pressure
Relief Duct

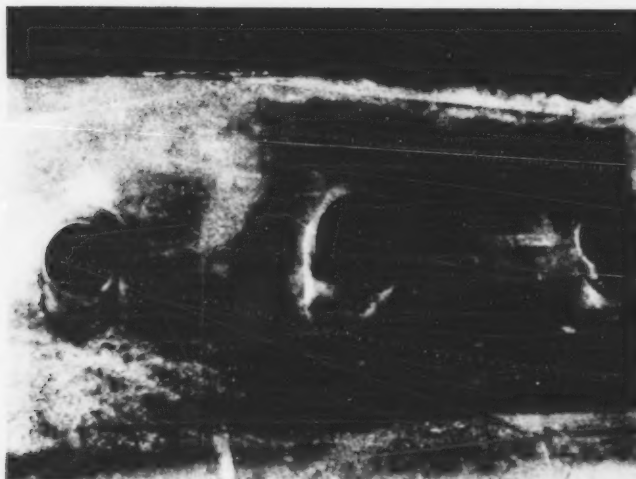
A



C



B



D



is of Rubber Flow
ompression Loading
Length of Sealing
Vacuum Boundary of
f Valve, Pressure
NGS.



Note: Views A and B show tears
propagating into flowed rubber.
View C shows rubber flow in opposite
directions for adjacent bolt holes,
whereas view D shows rubber flow
in same direction.

APPENDIX 4

Data for Thickness Of Flanges On Lower Diaphragm From
No 10 Pressure Relief Valve, Pressure Relief Duct,
Bruce A. NGS.

Measurement Number	Flange Thickness, mm					For Adjacent And Between Holes
	Inner Flange		Outer Flange			
	Adjacent To Holes	Between Holes	Adjacent To Holes	Between Holes	On Flowed Rubber	
1	7.37	6.83	7.09	7.01	8.66	-
2	6.93	6.38	7.19	7.19	8.66	-
3	6.99	6.63	7.37	7.37	8.97	-
4	6.81	7.26	7.39	7.44	8.69	-
5	7.16	6.93	7.06	7.29	9.04	-
6	6.10	7.06	7.39	7.32	8.51	-
7	7.09	6.73	7.42	7.24	9.40	-
Mean $\bar{X}$	6.92	6.83	7.27	7.27	8.85	7.07
Standard Deviation:						
σ_N	0.374	0.267	0.143	0.129	0.307	0.319
σ_{N-1}	0.404	0.289	0.155	0.139	0.284	0.325
N	7	7	7	7	7	28

Mean Height of Mound of Flowed Rubber = $8.85 - 7.07 = 1.78$ mm

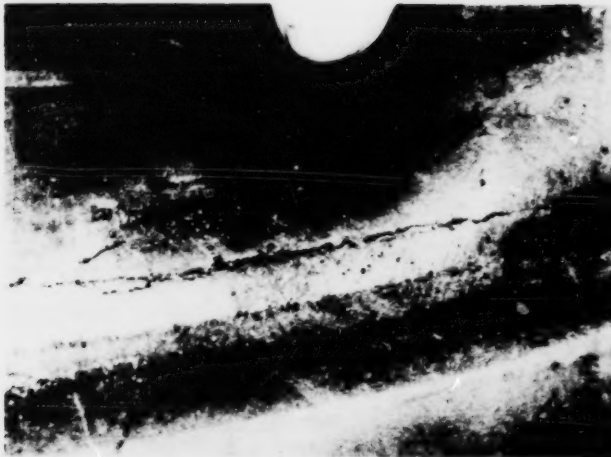
APPENDIX 5

Data For Distance From Inner Edge of Bolt
Hole To Vacuum Boundary at Bent Edge of Flanges, mm,
on Lower Diaphragm From No. 10 Pressure Relief
Valve, Pressure Relief Duct, Bruce A. NGS.

Measurement Number	Inside Flange	Outside Flange
1	13	19
2	13	19
3	11	20
4	13	19
5	11	19
6	13	19
7	13	17
8	14	17
9	11	15
10	13	15
11	14	15
12	15	15
13	13	19
14	13	20
15	12	20
16	13	20
17	14	20
18	14	21
19	10	20
20	11	19
21	14	19
-		
X	12.8	18.4
ON	1.27	1.89
ON-1	1.30	1.94

Photogr
In P
Pressure Relie

A



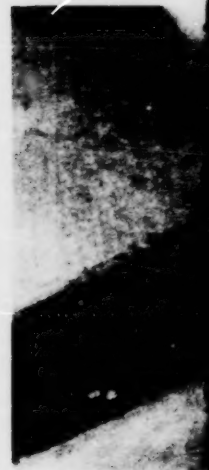
C



B



D

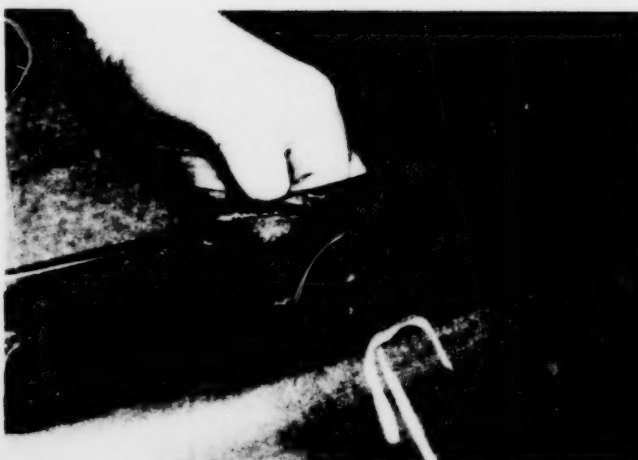


APPENDIX 6

Mechanical Impact Damage
of Diaphragms From No 10
Pressure Relief Duct, Bruce A. NGS



E

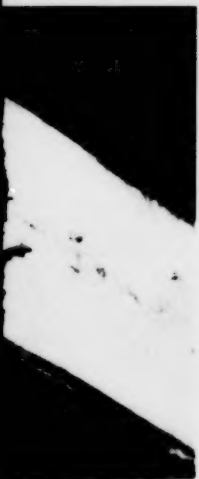


Note: Photograph A also shows
cracking attributed to ozone,
compression flow, set and
splitting. Photographs D and E
also show bolt holes with
evidence of minor leakage trails.

Photographs Illustrating
and Reduction in Stress
Diaphragms From
Pressure Re



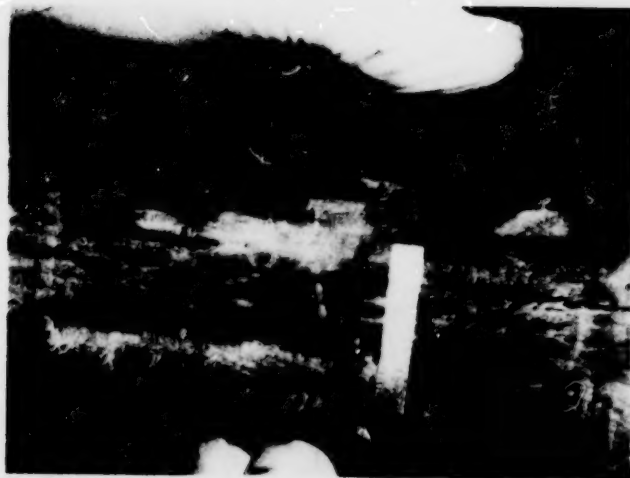
Edge
ges of
alve,



APPENDIX

Photographs Showing Surface
to Atmospheric Ozone and to
Adjacent Rubber Junctions
Diaphragms From No 10 Pressure
Relief Duct, Br

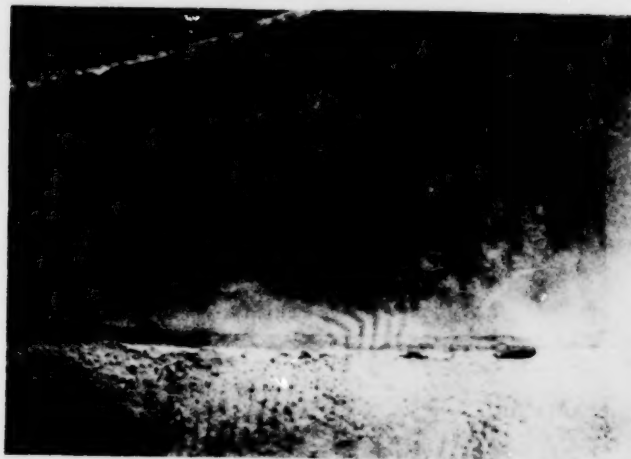
A



C



B



D

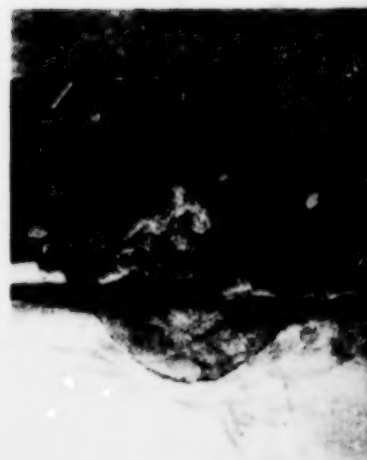
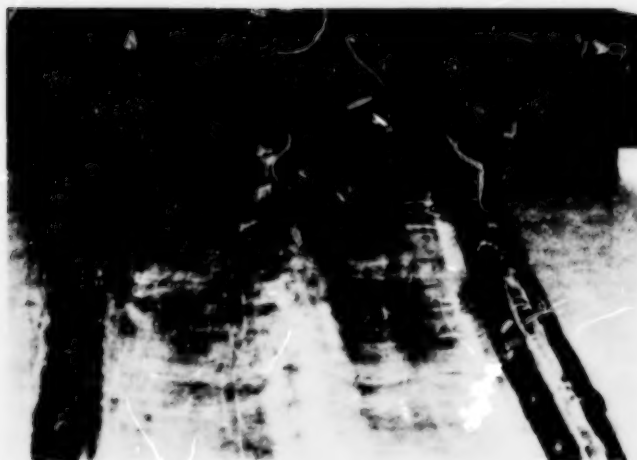


as Attributed
e Fusion of
ufacture of
lve, Pressure

A. Separations attributed to ozone.

B., C. and D. Separations attributed
to poor knitting of
gum stock prior to cure.

AL
Photographs Showing Leaks
Across Flanges And Obliteration
Bend of Diaphragms From
Pressure Relief



ills From Containment
of Moulded Corners At
Pressure Relief Valve,
Bruce A NGS.



Data For Du
D-Shaped Se
No. 10. P

Measurement Number	Durometer Hardness REX A. ASTM D 2240
-----------------------	--

1	47
2	57
3	49
4	47
5	52
6	47
7	48
8	46
9	57
10	48
11	49
12	48
13	50
14	49
15	50
16	49
17	49
18	49
19	49
20	50
21	51

Mean $\bar{X}$

49.6

Standard Deviation:

σ_N

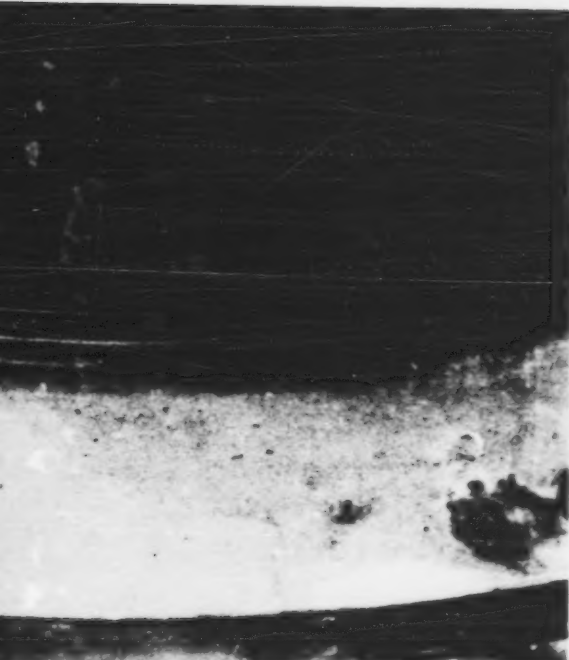
2.77

σ_{N-1}

2.84



s And View of Vacuum
ressure Relief Valve
uct. Bruce A. NGS.



A



B

View of D-shaped neoprene seal in bottom casing of pressure relief valve.

Close-up view of central indentation from seating foot at centre of the exposed surface of the seal.

APPENDIX 11

Data For Durometer Hardness And View of
Contact Impressions in Neoprene Upper Bumper R
In No. 10 Pressure Relief Valve, Pressure
Relief Duct, Bruce A. NGS.

Measurement Number	Durometer Hardness REX A, ASTM D 2240
1	48
2	46
3	43
4	49
5	47
6	47
7	48
8	49
9	45
10	46
11	47
12	48
13	47
14	49
15	48
16	47
17	47
18	46
19	49
20	45
21	48

Mean $\bar{X}$ 47.1

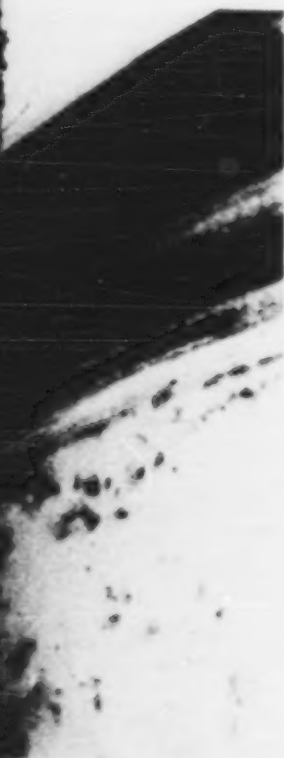
Standard Deviation:

σ_N 1.50
 σ_{N-1} 1.58



View of contact impressi
of pressure relief valve
the blade seat in the D
indicate a variation in
of the inner edge of the

s And View of
Upper Bumper Ring
valve, Pressure
A. NCS.



contact impressions left on bumper ring by piston bumper
relief valve. Unlike the single impression made by
seat in the D seal to vacuum, these impressions
a variation in the impact position and possible chipping
inner edge of the rubber bumper on impact.

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